



Preparation, testing and performance of a TiO₂/polyester photocatalyst for the degradation of gaseous methanol

M.I. Mejía^a, J.M. Marín^a, G. Restrepo^a, L.A. Rios^a, C. Pulgarín^b, J. Kiwi^{b,*}

^a Applied Physicochemical Processes Group, Chemical Engineering Department, Antioquia University, Engineering College, Street 67 53-108, AA 1226, Medellín, Colombia

^b EPFL-SB-ISIC-GGEC, Station 6, Ecole Polytechnique Fédérale de Lausanne, 1015 Lausanne, VD, Switzerland

ARTICLE INFO

Article history:

Received 1 August 2009

Received in revised form 4 November 2009

Accepted 7 November 2009

Available online 11 November 2009

Keywords:

Sol–gel

Photocatalysis

Polyester–TiO₂

Methanol photodegradation

ABSTRACT

TiO₂ modified polyester photocatalysts were prepared by immersion, drying and curing of the polyester in TiO₂ containing suspensions under different experimental conditions. The structure of TiO₂ layers on the polyester varied according to the time of immersion and type of polyester used. The optical microscopy (OM) and scanning electron microscopy (SEM) show a more uniform distribution of TiO₂ on the polyester prepared by sol–gel as compared to the silicone as a binder. Energy diffuse spectroscopy (EDS) and infrared (ATR-FTIR) spectroscopy confirmed that TiO₂ bonded to the polyester textile. BET analysis showed that TiO₂–SiO₂ applied by sol–gel on polyester led to a higher surface area compared to silicon. Photodegradation of gaseous methanol mediated by the TiO₂–polyester was followed by gas chromatography (GC) and ATR-FTIR spectroscopy. The TiO₂–polyester sample prepared by sol–gel with an immersion time of 11 h exhibited the most favorable photocatalytic performance during methanol degradation in the gas phase. The best performance during methanol photodegradation was observed for the smallest agglomerate TiO₂ size. The structure–reactivity relationship for different photocatalysts was systematically explored. Quantitative evaluation of the cluster size, immersion time and catalyst loading provided the evidence for the best performance for methanol degradation by the catalyst prepared at 11 h immersion time. The photocatalytic activity of the TiO₂–polyester catalyst was observed to remain stable during methanol over several degradation cycles.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

TiO₂ has become a widely used photocatalyst employed in degradation of gaseous and liquid pollutants due to its low price, chemical stability and lack of toxicity [1,2]. Furthermore, TiO₂ is used in the preparation of many composites [3,4], self-cleaning [5,6] and bactericide [7,8] materials. Heterogeneous photocatalysis is a promising technology for the removal of VOCs like gaseous methanol. TiO₂ photocatalysts are commonly used in processes to degrade in the gas phase [9,10].

Volatile organic compounds (VOCs) constitute an important group of pollutants due to their toxicity and adverse biological effects. Methanol is used widely as the solvent in industry and also as raw material to prepare formaldehyde, anti-freezing solvents, fuels, in inks and in the preparation of dyes, resins and adhesives [11–15]. Methanol at 20 °C achieves quickly a harmful concentration in the air leading to irritation of the eyes, skin and respiratory problems. A prolonged exposure to methanol causes dizziness,

nausea, lack of coordination and drowsiness. Higher doses lead to unconsciousness and death [16].

A variation on the commonly used dip-coating method for the deposition of TiO₂ is presented in this study. Our approach focuses on the immersion time of the polyester in the TiO₂ suspensions. Subsequently these photocatalysts were tested during the degradation of methanol. Two immersion methods were used during the catalyst preparation [17–18]. The first method used silica sol–gel as a TiO₂ binder on the textile to avoid the corrosion of the polyester by the h⁺ holes produced by TiO₂ under light irradiation. The second method used silicon as a binding agent to protect the polyester textile.

Polyester is one of the most resistant low cost fabrics that have been coated for different uses by TiO₂ [1–4]. This textile presents a large surface area making it suitable as a substrate for photocatalytic applications [5–7].

The polyester fabrics have been chosen because they are flexible and stable materials produced in large quantities. In recent years, the modification of textiles by TiO₂ aiming at pollutant degradation and self-cleaning processes has been reported [19–21]. This textile presents a large surface area making it suitable as a substrate for photocatalytic applications [5–7]. This study reports the preparative conditions of TiO₂/polyester used at low temperatures for degradation of gaseous methanol.

* Corresponding author. Tel.: +0041 21 534 8261; fax: +0041 21 693 4111.
E-mail address: john.kiwi@epfl.ch (J. Kiwi).

2. Experimental

2.1. Materials

We used two types of 100% polyester fabrics: the first type, polyester PT is a polyester containing the additives necessary for ready textile use in the form of a cohesive yarn [22]. The second type, polyester PM, corresponds to a “non-woven fabric” and is typically manufactured by putting small polyester fibers forming a web without previous spinning or weaving [21,23]. Both types of polyesters were provided by local textile industries.

2.2. Polyester samples prepared using TiO_2 - SiO_2 sol-gel

The sol-gel of SiO_2 to impregnate the polyester was prepared using tetraethyl ortosilicate (TEOS), distilled water, isopropyl alcohol (ISO), and HCl 3 M. All chemicals were reagent grade (p.a.). The hydrolysis of TEOS leads to the substitution of OR groups linked to silicon by silanol Si-OH groups (Fig. 1a and b). These groups react to form Si-O-Si (siloxane), leading to three-dimensional networks (Fig. 1c). The isopropyl alcohol and ethanol formed during the process remained within the pores (Fig. 1d) [17–18]. After ageing for 24 h, a silica structure was formed. Then, TiO_2 Degussa P-25 was added and was trapped within the pores of silica matrix (Fig. 1d). The TiO_2 enters the SiO_2 matrix and remains catalytically active. This is shown below in this study during the degradation of methanol.

Subsequently the polyester sample was immersed into this TiO_2 - SiO_2 suspension and left for different times. Immersion times between 2 and 24 h were tested. Polyester samples having an area of 9 cm^2 were tested. The silica added on the polyester surface had two functions: (a) to serve as a binder for TiO_2 on the polyester textile and (b) to protect the polyester from the h^+ generated at the TiO_2 surface during light irradiation.

The aqueous dispersions were prepared using 15 ml TEOS, 25 ml of isopropanol, 2.4 ml H_2O , 0.1 ml HCl, 3 M and 3.6 g of TiO_2 . The coated samples were dried at 100°C , in air during 1 h (Fig. 2).

2.3. Polyester textiles prepared with TiO_2 - SiO_2 using silicone

Silicone employed as a binding agent was a poly-silicone and its molecular structure is shown in Fig. 3 and mediates the TiO_2 adherence to polyester. Silicone has been used widely as a binding agent.

The silicone dispersion was prepared by dilution of 0.84 g of silicone in 50.4 ml of dichloromethane under magnetic stirring. Then, 3.5 g of TiO_2 was added to the dispersion. The polyester fabric was immersed in the dispersion and left for different times between 2 and 24 h under stirring. Then, the coated samples were then dried in oven at 100°C for 1 h and washed thoroughly. Fig. 4 shows the procedure used in this study. The PT- and PM-polyesters impregnated with silicone presented a yellow color unlike the sol-gel coated with SiO_2 fabrics that were observed to be white. The coloration of the fabrics was a result of the oxidation of silicone leading to colored functional groups [23,24]. The yellow coloration of fabrics is not desirable for textiles for commercial textile applications.

The use of silicone in coatings was not further explored in this study since during methanol degradation the coated polyester delaminated due to the loss of TiO_2 - SiO_2 layers. For these reasons, the effect of the immersion time in photocatalytic evaluation was evaluated only for samples prepared by sol-gel. These films of TiO_2 - SiO_2 prepared by sol-gel did not delaminate during methanol degradation and the thin layers conserved the TiO_2 agglomerates.

2.4. Characterization of samples

Surface characterization of the SiO_2 - TiO_2 -PT aggregates on polyester was carried out by scanning electron microscopy (SEM)

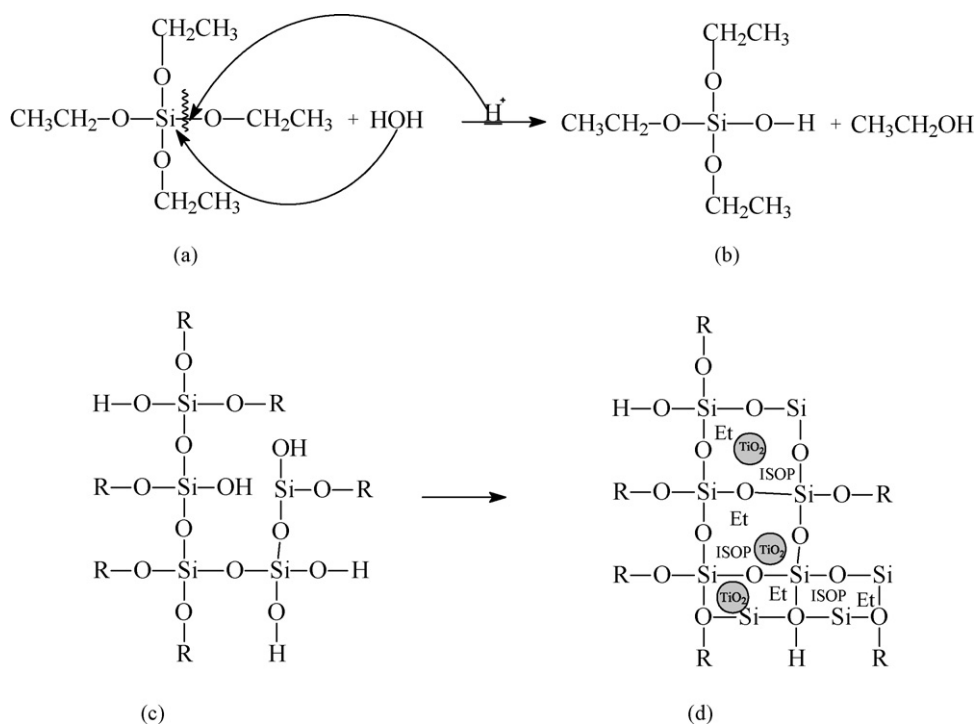


Fig. 1. Mechanism of silica matrix formation by sol-gel method and addition of TiO_2 Degussa P-25 (in the figure, a bi-dimensional view is displayed). (a and b) Substitution of OR groups linked to silicon by silanol Si-OH groups, (c) Si-OH groups react to form Si-O-Si (siloxane) bonds, (d) isopropyl alcohol (ISOP) and ethanol (ET) formed during the process remained within the pores, additionally TiO_2 Degussa P-25 is trapped within the pores after its addition.

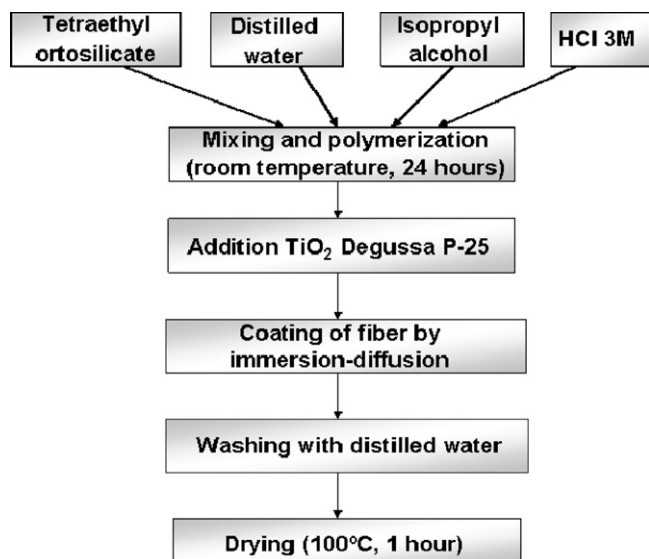


Fig. 2. Schematic of the sol-gel coating.

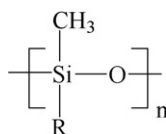


Fig. 3. Molecular structure of polysilicone employed in binding agent method.

by way of a JEOL JSM 5910LV field emission scanning electron microscope provided for with a BS-SE-detector and an energy dispersive spectrometer (EDS). Optical microscopy (OM) of the impregnated TiO₂ surface was carried out with a NICO E200 optical microscope.

The infrared spectroscopy was performed with an IR-Prestige-21/8400S Fourier Infrared Transform Spectrometer provided with an attenuated total reflectance (ATR-FTIR) attachment. The spectrum was taken in the range of 4000–500 cm^{−1}. The Ti-content on polyester fabrics was evaluated by X-ray fluorescence analysis by means of a PANalytical PW2400, RFX spectrometer. BET surface areas measurements of TiO₂-coated polyester were determined using N₂ physisorption at 77 K, with a Micromeritics Gemini V 2380 instrument. All the samples were out-gassed at 100 °C for 2 h in a Micromeritics Vac Preo 06 Kbars, prior to the

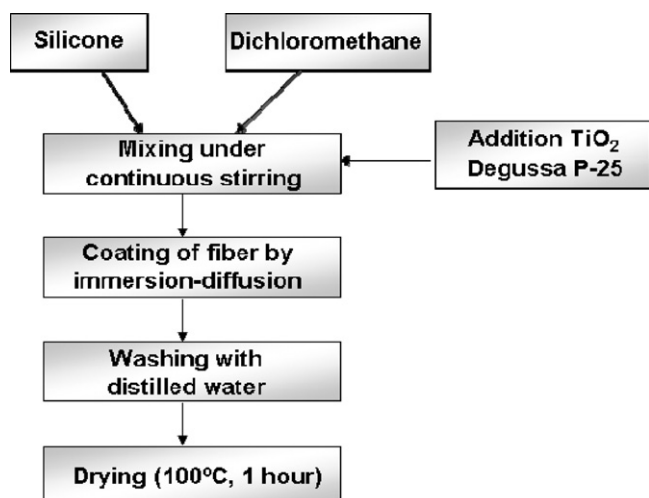


Fig. 4. Schematic of the process using silicone.

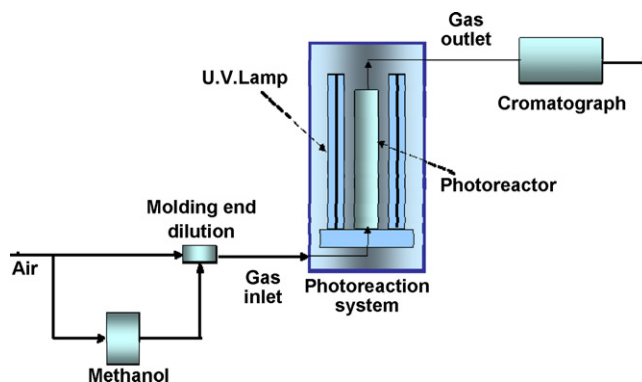


Fig. 5. Photodegradation unit of methanol.

surface area measurements. For BET analysis all the polyester fabric were used (9 cm²).

2.5. Photocatalytic evaluation of the fabrics

The photodegradation of methanol was carried out in a Pyrex flow tubular reactor (9 cm length, effective volume 50 ml, containing the TiO₂ coated fabric photocatalyst with an area of 9 cm²). Three UV lamps (light centered at 366 nm, 4 W) were positioned around the reactor and aligned in a concentric axial geometry at 120° of each other. The schematic diagram of the photodegradation unit is shown in Fig. 5. The flow is tangential to the photocatalyst media. The photocatalyst is placed on the inner surface of the inner cylinder, not on the outer surface. The airflow was split into two streams; the first flow (carrier flow) allowed dragging the methanol into the photoreactor. The contaminant was kept at −13° C in a cooling bath to control the spontaneous evaporation. The second airflow (the dilution flow) allowed diluting the methanol to reach the concentration range required for the experiments. 0.5 SCCM of carrier flow along 70 SCCM of the dilution flow were employed. The resulting flow was introduced into photoreactor and the methanol degradation was measured by gas chromatography.

The methanol peak in the chromatogram appeared after 2 min in the Agilent-6890N GC, using TCD (thermal conductivity detector) at 105 °C, EC-WAX column of 30 m × 0.25 μm × 250 μm mm at 55 °C and splitless mode injector at 80 °C. The chromatographic readings were taken every 8 min.

The photocatalytic decomposition percentage of methanol (%M_{phot}) was calculated by:

$$\%M_{\text{phot}} = \frac{C_0 - C}{C_0} \times 100$$

where C₀ is the initial concentration of methanol, and C is the residual photoreactor concentration of methanol after 200 min of photocatalysis. The initial concentration of methanol (C₀ concentration) was measured when polyester was completely saturated. This avoids the effect of methanol absorption on the polyester when measuring the methanol photocatalytic degradation. In this case the decrease in the methanol concentration can be ascribed only to photodegradation.

3. Results and discussion

3.1. Optical microscopy

Optical microscopy images of the fabrics coated by immersion-diffusion at different times are presented next in Fig. 6. The size of the darker TiO₂ aggregates decreased with immersion times >2 h (Fig. 6a–c) up to 11 h. The distribution of the TiO₂ becomes more

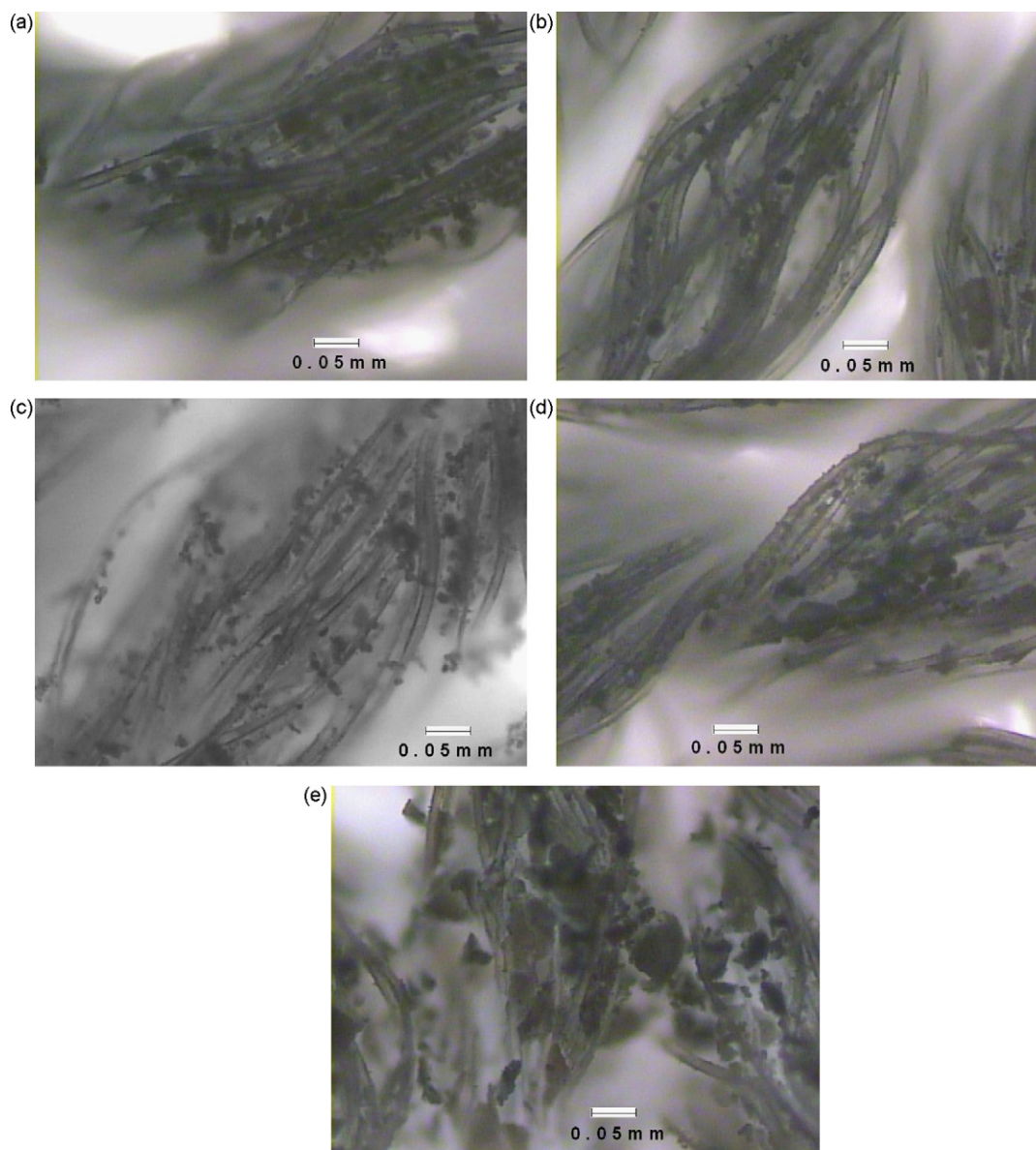


Fig. 6. Optical with 10 \times for TiO_2 - SiO_2 -polyester fabric prepared by sol-gel at immersion times of (a) 2 h, (b) 6.5 h, (c) 11 h, (d) 15.5 h and (e) 20 h.

uniform and smaller size agglomerates were observed at 11 h. After 11 h immersion (Fig. 6d and e), the size of the TiO_2 aggregates increases again showing some inter-particulate cracks. These cracks were observed to disappear during the methanol photo-degradation described in Section 3.7 below. In order to gain a more detailed and quantitative information of the TiO_2 size agglomerates we carried out SEM and the results are presented next in Section 3.2.

3.2. Scanning electron microscopy (SEM)

The scanning electron microscopy for several SiO_2 - TiO_2 -PT polyester samples with different immersions is shown in Fig. 7. The micrographs show widespread aggregation of TiO_2 particles covering the polyester surfaces. The information obtained considered more than 100 TiO_2 aggregates and show that the size of TiO_2 aggregates decrease with longer immersion times. The TiO_2 after 11 h immersion presented the more uniform TiO_2 -agglomerate distribution. At longer immersion times, the TiO_2 film thickness increased and the crack density was also observed to

increase on the polyester surface. Due to the type of preparation, it is probably the SiO_2 film thickness that increases and not the TiO_2 film as seen in Fig. 7(c).

Fig. 8 presents in more detail way the average size of agglomerates found on SiO_2 - TiO_2 -PT polyester samples impregnated at different times by sol-gel. It is noted that the size of agglomerates decreases with increased immersion time, reaching a minimum at 11 h. At 11 h, the agglomerates present a small size, revealing a slightly higher amount of SiO_2 than TiO_2 . At higher immersion times up to 24 h, the size of the agglomerates was observed to increase again.

3.3. Energy dispersive spectroscopy (EDS) analysis

The EDS results for SiO_2 - TiO_2 -PT polyester samples with 11 h immersion time show the presence of TiO_2 12.8%, C 22.1%, O 51.6% and Si 13.55%. These results indicate that TiO_2 was deposited on the polyester, the presence of C and O was due to the polyester surface. The signal due to Si (from tetraethyl ortosilicate TEOS) was also observed.

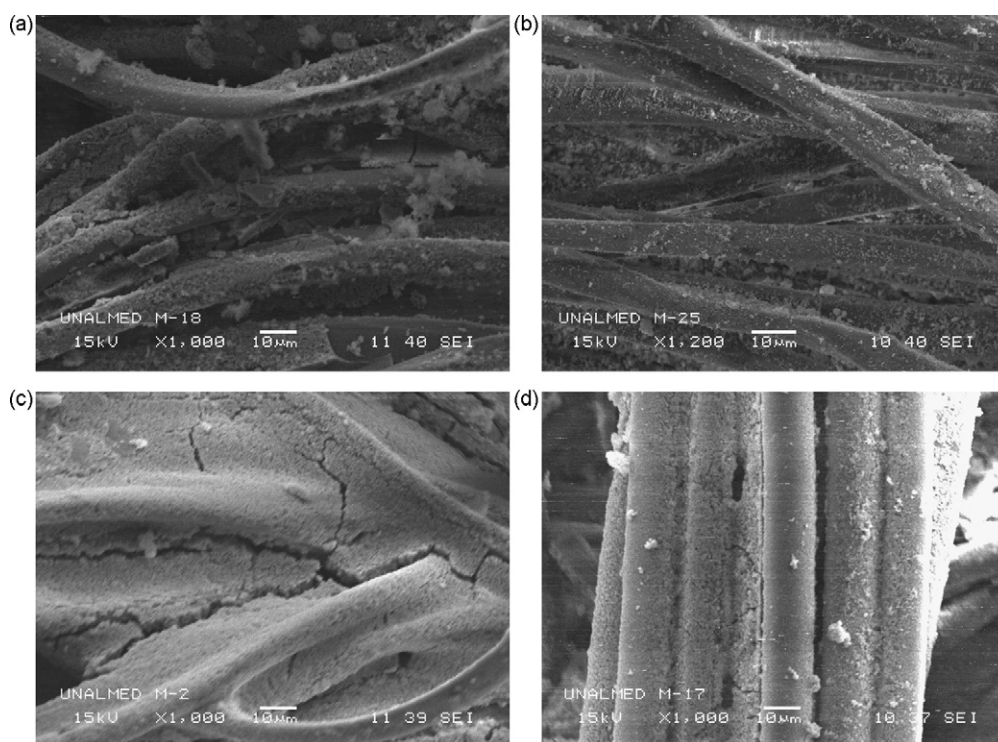


Fig. 7. SEM images of TiO_2 - SiO_2 -PT fabrics coated by sol-gel, after: (a) 2 h, (b) 11 h, (c) 15.5 h and (d) 20 h.

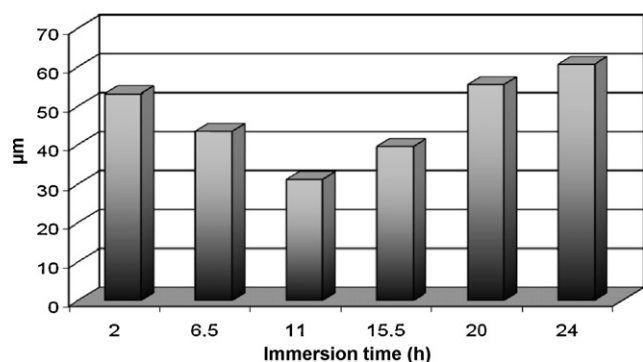


Fig. 8. Agglomerate sizes of TiO_2 - SiO_2 -PT polyester sample fabrics with different immersion times by sol-gel method.

3.4. X-ray fluorescence determination of TiO_2 -content on polyester

Additionally, by X-ray fluorescence the amounts of TiO_2 and SiO_2 on SiO_2 - TiO_2 -PT polyester samples prepared by sol-gel were determined. The results are shown in Fig. 9. The average error in

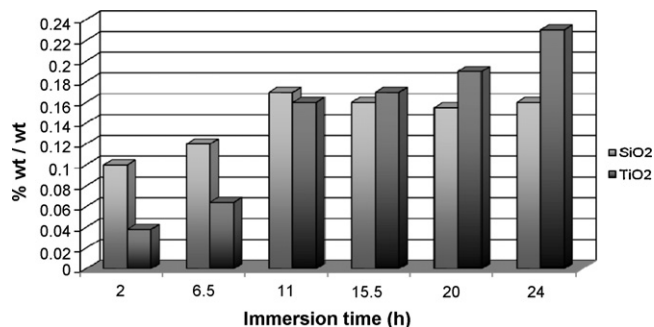


Fig. 9. X-ray fluorescence percentage by fabrics with different impregnation times by sol-gel method: gray columns wt%/wt% SiO_2 ; black columns wt%/wt% TiO_2 .

Table 1

BET area for diverse polyester catalysts used in the degradation of methanol.

Fabric	BET area (m^2/g) (11 h)	BET area (m^2/g) (24 h)
PT (sol-gel method)	52.9 ± 2.5	54.2 ± 1.7
PT (silicone binder)	5.6 ± 0.1	8.9 ± 0.2
PT non-loaded	0.2 ± 0.03	

the results reported in Fig. 9 was 6–7% taking 3 samples from each material. Samples with immersion times up to 11 h increase in % TiO_2 loading compared with samples obtained with lower immersion times. For higher immersion times, the % TiO_2 found in agglomerates is greater than the % SiO_2 due to the increased differential absorption of TiO_2 within the immersion time.

3.5. BET surface areas measurements

Table 1 shows the results of BET surface area analysis for SiO_2 - TiO_2 -PT fabrics prepared by sol-gel and binding agent silicone with two different immersion times. The TiO_2 - SiO_2 -coated fabrics by sol-gel have an area much larger than when silicone was used and will be used from now on throughout this study. The high BET area for the SiO_2 - TiO_2 -PT fabric with respect to the one prepared using silicone and even more so to the polyester-PT non-loaded with TiO_2 or SiO_2 is clearly seen in Table 1.

3.6. Infrared spectroscopy of SiO_2 - TiO_2 -PT polyester samples (ATR-FTIR)

Fig. 10 shows the ATR-FTIR spectra of SiO_2 - TiO_2 -PT polyester samples after 11 h of immersion prepared by sol-gel. The ATR-FTIR spectrum shows the TiO_2 band in the range 800 – 500 cm^{-1} . The band at 987 cm^{-1} is associated to the stretching vibration of Si-OH or Si-O groups. Furthermore symmetric and asymmetric stretching bands of Si-O-Si were found at 1078 and 1030 cm^{-1} .

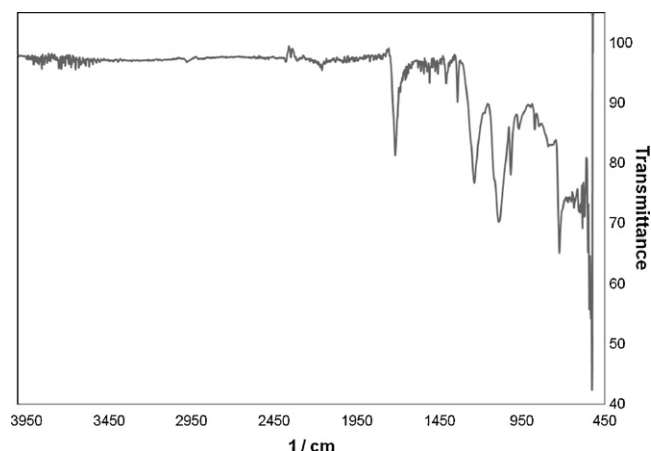


Fig. 10. ATR-FTIR spectra for the polyester fabrics $\text{TiO}_2\text{-SiO}_2\text{-PT}$ after 11 h immersion by sol-gel method.

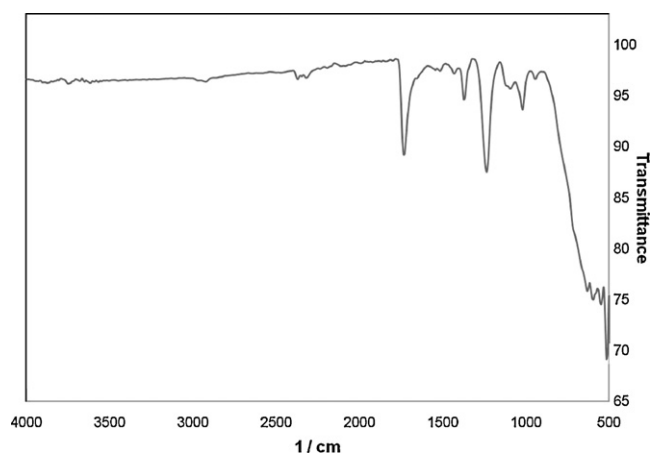


Fig. 11. ATR-FTIR spectra for the polyester $\text{TiO}_2\text{-silicon-PT}$ after 11 h immersion.

respectively [25,26]. The presence of the latter band confirms that SiO_2 was formed during TEOS hydrolysis.

Characteristics bands of polyester fibers were also observed. Peaks associated with saturated esters were found at 1729 cm^{-1} due to carbonyl (-C=O) stretching. The bands around $1330\text{--}1240$ and $1160\text{--}1080\text{ cm}^{-1}$ arise from ester group vibrations [26]. Additionally, -C-H bonds associated with the benzene ring in the polymer structure show overtones peaks around $1600\text{--}1400\text{ cm}^{-1}$ with the out-of-plane benzene ring C-H bands at 1018 , 875 and 730 cm^{-1} [27].

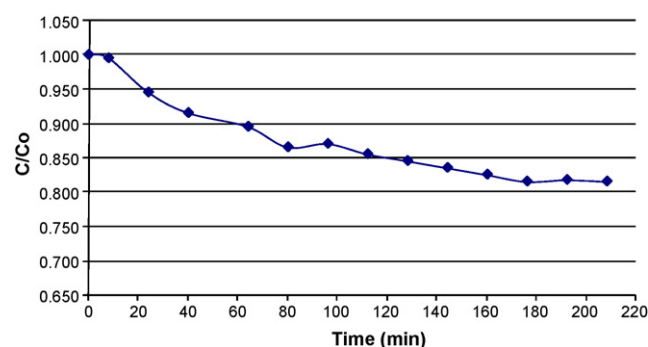


Fig. 12. Concentration vs. time during a methanol degradation cycle using $\text{TiO}_2\text{-SiO}_2\text{-PT}$ polyester fabrics prepared by sol-gel and with immersion time 11 h.

Table 2

Methanol degradation cycles on $\text{TiO}_2\text{-SiO}_2\text{-PT}$ polyester sample prepared with 11 h of immersion by sol-gel.

Photodegradation cycle	% M_{phot}	Photodegradation time (minutes)
Cycle 1	18.55%	208
Cycle 2	18.56%	184
Cycle 3	19.10%	224
Cycle 4	17.98%	232
Cycle 5	18.68%	200
Cycle 6	18.31%	208

Table 3

Methanol degradation at 11 and 24 h impregnation time with two types of fabrics.

Fabric	% M_{phot} (11 h)	% M_{phot} (24 h)
PT (sol-gel)	18.55%	14.07%
PM (sol-gel)	14.86%	13.74%
PT (binding agent)	15.81%	11.43%
PM (binding agent)	14.13%	13.62%

The IR of polyester $\text{TiO}_2\text{-silicon-PT}$ samples with 11 h immersion time are presented in Fig. 11, showing polyester fiber bands and also TiO_2 bands between 800 and 500 cm^{-1} . Silicone bands of the methyl silicone at 1728 cm^{-1} corresponding to -C=O stretching of ester radicals on the silicone samples are shown in Fig. 11. $\text{Si}(\text{CH}_3\text{-Si})\text{CH}_3$ - asymmetric and symmetric stretchings of $\text{Si}(\text{CH}_3\text{-Si})$ were observed at 1365 and 1226 cm^{-1} as well as the silicone bands at 1118 and 1018 cm^{-1} due to Si-O-Si stretching vibrations [27–29].

3.7. Photocatalytic methanol degradation

The concentration of methanol vs. time during irradiation (% M_{phot}) on $\text{SiO}_2\text{-TiO}_2\text{-PT}$ polyester is shown in Fig. 12 showing a decrease in the methanol concentration of up to 200 min, when a plateau was reached.

Six different methanol degradation cycles were carried out successively with the same sample to test the reproducibility of methanol degradation. Results are presented in Table 2. The $\text{TiO}_2\text{-SiO}_2\text{-PT}$ sol-gel sample immersed for 11 h was employed in these cycles. The results indicate a stable catalytic activity for the photocatalyst used. X-ray fluorescence determination of TiO_2 -content on the polyester show that at time zero (before the start of the photodegradation of methanol) the fabric had a loading of 0.16 wt/wt TiO_2 and after six cycles the TiO_2 was 0.13% (Fig. 9).

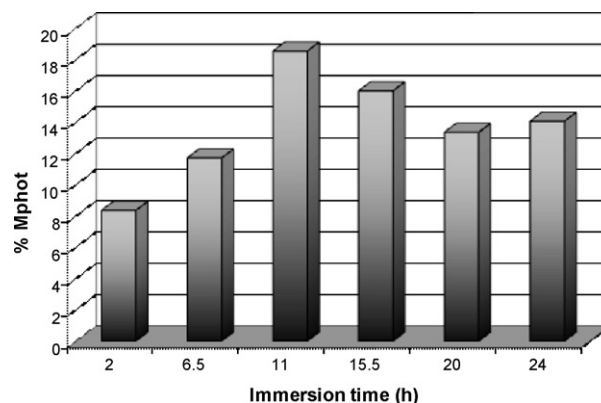


Fig. 13. Methanol degradation percentage using $\text{TiO}_2\text{-SiO}_2\text{-PT}$ polyester fabrics as photocatalyst prepared by sol-gel.

There is a small loss of TiO₂ during the methanol degradation confirming the stability of this catalyst.

Table shows the methanol degradation percentage for the two types of fabrics PT and PM by sol–gel (the first two rows) and binding agent method (the last two rows). Methanol degradation percentages of the fabrics with immersion of 11 and 24 h are shown in Table 3.

The PT sol–gel based photocatalyst lead to a higher degradation of methanol due to a more homogeneous TiO₂ film and a lower film delamination.

The effect of the different immersion times on the methanol degradation is presented in detail in Fig. 13. The conversion rate was calculated for the methanol concentration reaching a plateau at ~200 min. The increase of immersion time up to 11 h causes a greater amount of methanol to be degraded due to the increased TiO₂ presence on the polyester surface relative to immersion times of 2 and 6.5 h. At 11 h immersion time, the TiO₂ agglomerates attain a small size (Fig. 8). Concomitantly, Fig. 9 shows that the TiO₂ loading on the polyester for this sample is relatively high. At longer immersion times, the size of the agglomerated increases (Fig. 8) as the TiO₂ deposited increases, but the catalytic activity for methanol decomposition decreases (Fig. 13). This means that a TiO₂–SiO₂–PT sol–gel sample immersed for 11 h presents the highest amount of TiO₂ sites held in exposed positions available to interact with methanol in the photoreactor. At 11 h immersion time, there was an optimal ratio of TiO₂/cluster size effective in methanol decomposition. At longer immersion times, the TiO₂ dispersion decreases due to the agglomeration of TiO₂ on the polyester fabric.

4. Conclusions

- A strong dependence between the time of immersion and the structure of the TiO₂ surface agglomerates on the polyester surface was observed. The polyester immersed for 11 h in sol–gel presented the most uniform distribution, smaller aggregate size and highest photocatalytic activity. Longer immersion times lead to bigger agglomerates decreasing the reactivity towards methanol degradation in spite of a slight increase in the TiO₂ loading on the polyester.
- Similar methanol photodegradation kinetics was reached up to six successive cycles by using a TiO₂–SiO₂–PT polyester sample obtained by sol–gel.
- The TiO₂–polyester coated using silicone binder lead to less effective methanol degradation.

Acknowledgements

The authors thank COLCIENCIAS and the University of Antioquia for financing the project. We thank for the help of J-M Lavanchy, IMG-Centre d'Analyse Minerale, Bat Anthropole, Univ-Lausanne, CH-1025, Lausanne, Switzerland with the X-ray fluorescence and to S. Arroyave and C. Sanchez, PFA group, Medellín, Colombia for the help with the BET measurements.

References

- [1] A. Mills, S. LeHunte, J. Photochem. Photobiol. A 108 (1997) 1–16.
- [2] M.R. Hoffmann, S.T. Martin, W.Y. Choi, D.W. Bahnemann, Chem. Res. 95 (1995) 69–94.
- [3] A. Fujishima, K. Hashimoto, T. Watanabe, TiO₂ photocatalysis, in: *Fundamental and Applications*, Bkc Inc., Tokyo, 1999.
- [4] J. Winkler, Titanium Oxide, Vincentz, Hannover, 2003.
- [5] A. Bozzi, T. Yuranova, J. Kiwi, J. Photochem. Photobiol. A 108 (1997) 1–16.
- [6] W.S. Tung, W.A. Daoud, Acta Biomater. 172 (2005) 27–34.
- [7] D. Gumy, C. Morais, P. Bowen, C. Pulgarin, S. Giraldo, R. Hajdu, J. Kiwi, Appl. Catal. B 63 (2006) 76–84.
- [8] V. Nadochenko, N. Denisov, O. Sarkisov, D. Gumy, C. Pulgarin, J. Kiwi, J. Photochem. Photobiol. A 181 (2006) 401–407.
- [9] Z. Liuxue, I. Peng, S. Zhixing, Math. Chem. Phys. 98 (2006) 111–115.
- [10] J.M. Herrmann, Top. Catal. 34 (1–4) (2005) 49–65.
- [11] S.C. Kim, W.G. Shim, Appl. Catal. B: Environ. 79 (2008) 149–156.
- [12] L. Yang, Z. Liu, J. Shi, H. Hu, W. Shangguan, Catal. Today 126 (2007) 359–368.
- [13] Y. Hou, L. Wu, X. Wang, Z. Ding, Z. Li, X. Fu, J. Catal. 250 (2007) 12–18.
- [14] M.P. Paschoalino, J. Kiwi, W.F. Jardim, Appl. Catal. B: Environ. 68 (2006) 68–73.
- [15] R.J. Nelson, C.L. Flakker, D.S. Muggli, Appl. Catal. B: Environ. 69 (2007) 189–195.
- [16] R. Kavet, K.M. Nauss, Crit. Res. Toxicol. 21 (1990) 21–50.
- [17] M.I. Mejía, J.M. Marín, G. Restrepo, L.A. Ríos, Scientia et Technica 36 (2007) 97–102.
- [18] H. Schmidt, M. Mennig, Wet Coating Technologies for Glass. <http://www.solgel.com/articles/Nov00/mennig.htm>, 2006 (accessed May 2006).
- [19] Y. Dong, Z. Bai, R. Liu, T. Zhu, Atmos. Environ. 41 (15) (2007) 3182–3192.
- [20] H. Wang, Z. Wu, W. Zhao, B. Guan, Chemosphere 66 (2007) 185–190.
- [21] Y. Dong, Z. Bai, R. Liu, T. Zhu, Catal. Today 126 (2007) 320–327.
- [22] http://plutarco.disca.upv.es/~jcperez/doctorado/SV2D3DPI/trabajos/SectorTextil_2/Necesidades.htm, 2009 (accessed April 2009).
- [23] M.A. Angulo-Luna, March 2006. http://sisbib.unmsm.edu.pe/bibvirtualdata/Tesis/Ingenie/angulo_lm/angulo_lm.pdf.
- [24] W.G. Penney, The theory of molecular structure. IOPscience, Rep. Prog. Phys. 6 (1939) 212.
- [25] R. Peña-Alonso, F. Rubio, J. Rubio, J. Oteo, Boletín de la Sociedad Española de Cerámica y Vidrio 44 (2005) 387–392.
- [26] K.C. Cole, H. Ben Daly, B. Sanschagrin, K.T. Nguyen, A. Ajji, Polymer 40 (1999) 3505–3513.
- [27] WCASLAB. FTIR. <http://www.wcaslab.com/TECH/tbftir.htm>, 2009 (accessed May 2009).
- [28] D.A. Skoog, F.J. Holler, T.A. Nieman, Instrumental Analysis, vol. 5a, McGraw Hill, Madrid, 2001.
- [29] I. Skeist, Handbook of Adhesives, vol. 2, Van Nostrand Reinhold, New Jersey, 1977, p. 921.